

# In-Situ Synthesis and Characterization of Carbon Dots and TiO<sub>2</sub> Nanocomposites Anchored on TiO<sub>2</sub> Nanotube Arrays

Fan Li<sup>1\*</sup>, Yumei Pan<sup>2</sup>, Changjun Liu<sup>1</sup>, Chunlai Wang<sup>1</sup>, Kun Yang<sup>1</sup> and Feng Tian<sup>1\*</sup>

<sup>1</sup>Institute of Medical Equipment, Academy of Military Medical Sciences, Tianjin 300161, China.

<sup>2</sup>School of Medical Imaging, Tianjin Medical University, Tianjin 300203, China  
Email: vanadium\_1981@163.com

**Abstract.** A modified anodic oxidation method was used to prepare amorphous titanium dioxide nanotube arrays (TiO<sub>2</sub>NTs) on Ti foil firstly. Then TiO<sub>2</sub>NTs were decorated with nanocomposites of CDs-TiO<sub>2</sub> through designed one-step solvothermal techniques in-situ, accompanying with crystallization of TiO<sub>2</sub>NTs. The crystallinity of TiO<sub>2</sub>, morphologies and ingredients of the hybrid nanocomposites could be controlled by solvothermal conditions. It was found solvothermal procedure could play a similar role on the TiO<sub>2</sub> crystal formation like the common anneal treatments. Furthermore, there were more Ti-C bonds found in the composites derived from amorphous TiO<sub>2</sub>NTs undergone a solvothermal process. The measurements of photo-degradation on both methyl blue and rhodamine B showed an excellent photocatalytic activity for CDs-TiO<sub>2</sub> decorated TiO<sub>2</sub>NTs (CDs-TiO<sub>2</sub>-TiO<sub>2</sub>NTs) under no matter ultraviolet or visible light irradiation.

## 1. Introduction

Due to its low cost, high chemical stability and high photocatalytic activity, titanium dioxide (TiO<sub>2</sub>) has received considerable attention among semiconductor photocatalysts [1]. Up to now, various applications have been realized using TiO<sub>2</sub> based nanocomposites in water splitting [2-4], pollutants degradation [5-8], solar cells [9,10], gas sensors [11,12], and tumor therapy [13]. Besides the most common TiO<sub>2</sub> nanoparticles, various one dimensional TiO<sub>2</sub> nanostructures, such as nanowires [2, 14], nanorods [15], nanotubes [16-18], and nanofibers [19], have been developed for photoelectrochemical (PEC) applications. Those one dimensional TiO<sub>2</sub> nanostructures could offer a continuous pathway for photo-generated electrons to transport along their long axis so that to achieve an enhanced charge collection efficiency [20]. The vertically oriented TiO<sub>2</sub> nanotube arrays (TiO<sub>2</sub>NTs), which was first synthesized by Grimes in 2001 [21], have attracted considerable attention due to their highly ordered array structure, good mechanical strength, high specific surface area, facile synthesis process and fast charge transport properties. Since then, a great amount synthesis approaches for TiO<sub>2</sub>NTs had been developed [22].

However, all the pure TiO<sub>2</sub> materials had an inherent defect: the wide band gap (3.2 eV for anatase and 3.0 eV for rutile), which limits its response to the ultraviolet (UV) light only, leaving 95-97% energy of the whole solar spectrum unusable. Great efforts have been made to modify TiO<sub>2</sub> so as to improve its photo response capability. Among them, the doping processes had been proved to be useful in heightening the photocatalytic performance of under visible light, especially for the carbon materials used as dopants [23]. Carbon dots (CDs), a novel and eco-friendly carbon nanomaterial with tunable photoluminescence (PL) [24], were proved to be an excellent dopant for TiO<sub>2</sub>. Kang et al.



confirmed that photoelectrochemical hydrogen generation could be finished by graphite-derived CDs [25]. Those reports indicated that CDs are promising candidates for photocatalytic applications too. Lee et al. firstly explored the availability of  $\text{TiO}_2/\text{CDs}$  hybrids for the efficient photo-degradation of methyl blue [26]. Then Ho's results showed the  $\text{H}_2$  evolution rate of  $\text{TiO}_2/\text{CDs}$  nanocomposites was 9.7 times higher than that of bare  $\text{TiO}_2$  [27]. Likewise, Martins et al. found that the photo-oxidation rate of NO under UV and visible light using composite of  $\text{TiO}_2$  (P25) and N-doped carbon quantum dots was much higher than that of pure P25 [28].

Generally, an anneal process must be carried out for  $\text{TiO}_2\text{NTs}$  to realize the conversion from amorphous state to crystalline phase. And what's more, sometimes another hydrothermal or doping process were required to combine the as-prepared CDs with  $\text{TiO}_2\text{NTs}$ , such as the work finished by Su et. al [29]. Surely the complex technique was adverse to the practical application of  $\text{TiO}_2\text{NTs}$  composites. In this work, a modified anodic oxidation method was used to prepare amorphous  $\text{TiO}_2\text{NTs}$  firstly. Then nanocomposites of CDs and  $\text{TiO}_2$  were anchored on  $\text{TiO}_2\text{NTs}$  in-situ through a designed one-step solvothermal technique. The crystallinity of  $\text{TiO}_2$ , morphologies and ingredients of the nanocomposites could be adjusted by the solvothermal processes. Furthermore, methyl blue (MB) and rhodamine B (RB) were chosen to test the photocatalytic activity of different  $\text{TiO}_2\text{NTs}$  composites under UV light and visible light irradiation.

## 2. Material and Methods

### 2.1. Chemicals and Reagents

Ti foli (99.9%, thickness: 0.3mm), was supplied by Ruiboxing reagent company. Citric acid (99.5%), sodium fluoride (98%) and ethylenediamine (98%) were purchased from Alfa Aesar. Methylene blue (MB, 98.5%), rhodamine B (RB, 99%), tetrabutyl titanate (99%), triethanolamine (85%) and ethanol (99.7%) were obtained from GuangFu Technology Development CO, LTD. All other reagents were of analytical grades and used without further purification.

### 2.2. Preparation of $\text{TiO}_2\text{NTs}$ Composites

$\text{TiO}_2\text{NTs}$  were fabricated by a modified anodization process. Prior to anodization, the Ti foils were first degreased by sonicating in acetone, ethanol and DI water, respectively, followed by drying in air. Then the anodization process was carried out with a Ti foil as the anode and another Ti foil as the cathode in a 0.1M NaF and 0.5M  $\text{NaHSO}_4$  aqueous solution for 180 min at 20 V using a DC power supply. Finally, the as-prepared samples (anode) were rinsed in deionized water and dried with an air stream. The preparatory samples were marked as  $\text{TiO}_2\text{NTs-0}$ .

The preparation of nanocomposites of CDs and  $\text{TiO}_2$  ( $\text{CDs-TiO}_2$ ) was finished according to our previous reports [30]. As to  $\text{TiO}_2\text{NTs}$  decorated with  $\text{CDs-TiO}_2$  ( $\text{CDs-TiO}_2\text{-TiO}_2\text{NTs}$ ), the reaction solution was a mixture of 1.5 g citric acid, 0.2 ml triethanolamine and 10 ml tetrabutyl titanate in 60 ml ethanol. The ready amorphous  $\text{TiO}_2\text{NTs-0}$  was immersed in the solution with a sonication for 30 min to drive the solution into the nanotubes. Then a hydrothermal procedure was applied in a Teflon-lined stainless steel autoclave at 200 °C for 6 hours. After the autoclave was cooled to room temperature naturally, the products were washed with ethanol and water in turns for five times and dried at 80 °C in a vacuum oven overnight.

Simultaneously, to gain a better understanding of the role of one-step solvothermal technique on the formation of  $\text{TiO}_2\text{NTs}$  composites, parallel experiments were also carried out: the amorphous  $\text{TiO}_2\text{NTs-0}$  after anodization was firstly annealed at 450 °C in air for 2h, which was marked as  $\text{TiO}_2\text{NTs-450}$ .

### 2.3. Characterizations

UV-Vis absorption was measured on a DR 5000 UV-Vis spectrophotometer (HACH, America). The morphology and microstructure of the samples were examined by scanning electron microscopy (SEM) on a LEO 1530VP scanning electron microscope with an acceleration voltage of 20 kV. The surface states and composition of the composites were measured on a Kratos AXIS Ultra DLD X-ray Photoelectron Spectroscopy (XPS, Shimadzu, Japan). X-Ray diffraction (XRD) profiles of the

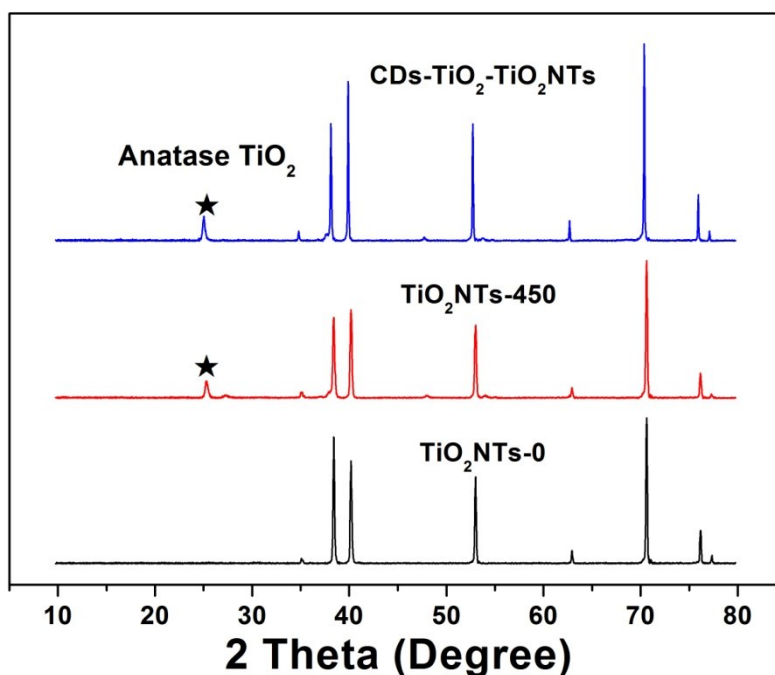
prepared samples were recorded on a Rigaku-D/MAX 2500 diffractometer (Rigaku, Japan) equipped with graphite monochromatized  $\text{CuK}\alpha$  ( $\lambda=0.15405$  nm) radiation at a scanning speed of  $4^\circ \text{ min}^{-1}$  in the range from  $10^\circ$  to  $80^\circ$ .

#### 2.4. Photocatalytic Measurements

The photocatalytic activity of all samples was tested under UV light or halogen lamp irradiation. MB and RB solution with the same concentrations (10 ppm) was prepared in water. Typically,  $\text{TiO}_2\text{NTs}$  samples with same surface area ( $2 \text{ cm} \times 3 \text{ cm}$ ) were immersed in 8 ml MB solution (10 ppm) and followed by 120 min vibration in the dark to reach the adsorption-desorption equilibrium between MB and photocatalysts before irradiation. Then the above reaction system placed in a quartz cuvette was exposed to ultraviolet (UV) light with a wavelength of 254 nm and a power of 8 W (Spectroline XLE-1000/F, UV CROSSLINKER) at room temperature. Without stirring, the suspension was taken out at regular intervals and analyzed using a UV-Vis absorbance spectroscopy. The photo-degradation measurements on RB were executed in the same way but using a 200 W halogen lamp as the visible light source.

### 3. Results and Discussion

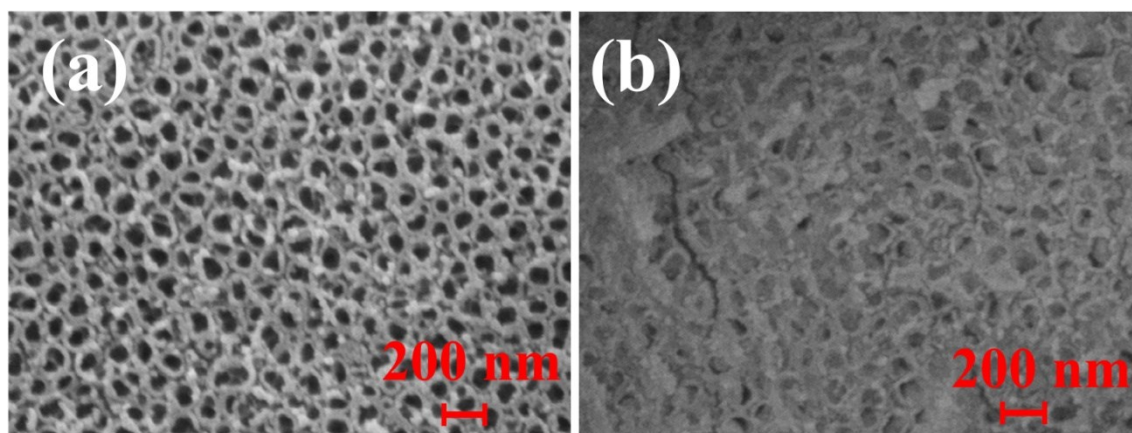
XRD was used to investigate the possible constituents and crystalline phase of  $\text{TiO}_2\text{NTs}$  composites prepared under different conditions. As shown in Figure 1, it is easy to find the existence of  $\text{TiO}_2$  as an imperfect crystal of anatase after solvothermal or anneal treatments. There were no  $\text{TiO}_2$  crystal signals for the initial  $\text{TiO}_2\text{NTs-0}$ . Once  $\text{TiO}_2\text{NTs-0}$  were further annealed at  $450^\circ \text{C}$  for 2h, the latter formed  $\text{TiO}_2\text{NTs-450}$  showed clear diffraction peak attributing to anatase  $\text{TiO}_2$ , which meant the successful construction of  $\text{TiO}_2$  nanotube arrays on Ti substrate by the anodization process, and finished transformation from amorphous state to crystalline phase. This result was consistent with the previous reports. And it's obvious that the solvothermal procedure could play a similar role on the crystal state transformation. In other words, solvothermal process could be a substitute for the common anneals technique.



**Figure 1.** XRD patterns for the Ti foil and different  $\text{TiO}_2\text{NTs}$  composites.

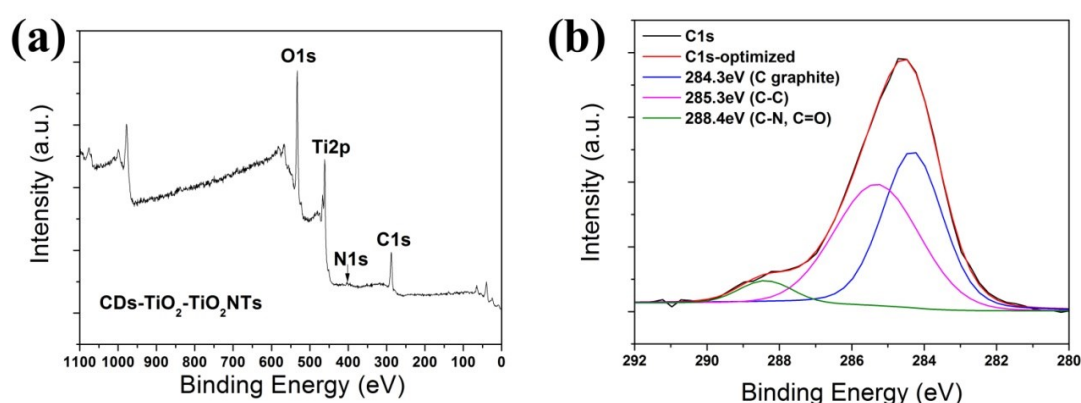
The microstructures and morphologies of as-prepared  $\text{TiO}_2\text{NTs}$  composites were probed using SEM (Shown in Figure 2). In the panoramic view, the  $\text{TiO}_2\text{NTs}$  samples were ordered nanotubes with

internal diameter around 80 nm. The nanotubes of TiO<sub>2</sub>NTs-450 were open. While the nanotubes in CDs-TiO<sub>2</sub>-TiO<sub>2</sub>NTs were full of tight CDs-TiO<sub>2</sub> nanocomposites. It's probably that the designed solvothermal processes played three roles on the initial TiO<sub>2</sub>NTs-0: production of CDs-TiO<sub>2</sub> in-situ, conversion of anatase TiO<sub>2</sub> from initial amorphous state, and tight connection between CDs-TiO<sub>2</sub> and TiO<sub>2</sub> nanotubes.



**Figure 2.** SEM micrographs of (a) TiO<sub>2</sub>NTs-450 and (b) CDs-TiO<sub>2</sub>-TiO<sub>2</sub>NTs.

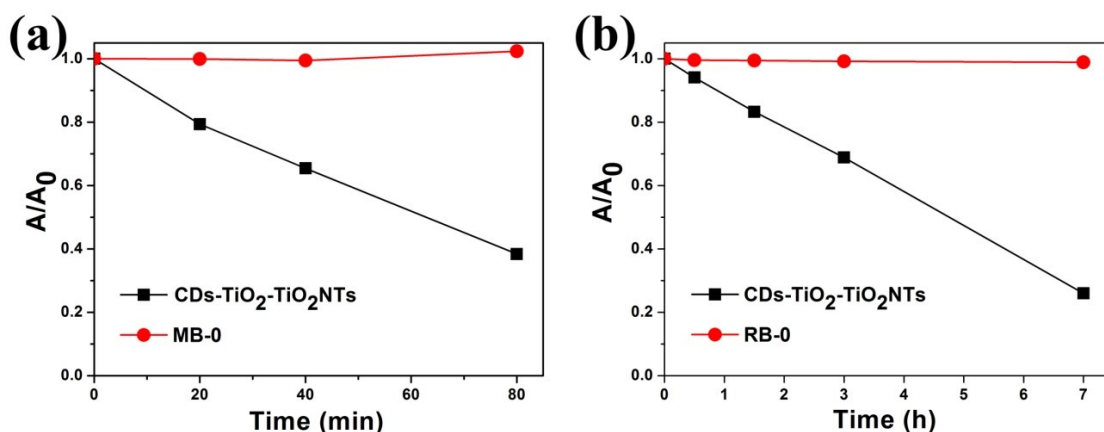
XPS was used to provide convincing evidences for the surface states and composition of the as-prepared TiO<sub>2</sub>NTs composites. The samples showed clear constituents of element C, O, N and Ti (**Figure 3**). It was probably that the carbon source was not only transformed into CDs, but also introduced to react with TiO<sub>2</sub>NTs-0 along with its crystallization. As to the high-resolution C 1s spectra of CDs-TiO<sub>2</sub>-TiO<sub>2</sub>NTs, the signal intensity of peaks at 284.3 eV and 285.3 eV were adjacent to each other, which meant a low carbonization degree. Meanwhile, taking the weakest TiO<sub>2</sub> crystal degree into account, It's easy to conclude that alcohol mediated solvothermal process was a bit adverse to either the formation of CDs or improvement of the TiO<sub>2</sub> crystal. Moreover, it's worth to note that the signal intensity in range from 281.3 eV to 282 eV corresponding to Ti-C bonds could be found in CDs-TiO<sub>2</sub>-TiO<sub>2</sub>NTs.



**Figure 3.** XPS spectra of CDs-TiO<sub>2</sub>-TiO<sub>2</sub>NTs: (a) whole, (b) high-resolution C 1s spectra.

In order to investigate the applied potentialities of the as-prepared TiO<sub>2</sub>NTs composites, we firstly evaluated their photocatalytic ability for the photo-degradation of MB under UV light (254 nm). Figure 4a plotted the UV-vis absorption at 664 nm of the reaction solutions at regular intervals, representing the photocatalytic ability of different catalysts. The intensity ratios of the absorbance at 664 nm after and prior to the UV light irradiation for a certain time ( $A/A_0$ ) were plotted as a function

of the reaction time. We can see that about 62% MB was degraded after 80 min UV irradiation for sample CDs-TiO<sub>2</sub>-TiO<sub>2</sub>NTs. As the CDs-TiO<sub>2</sub> composites had shown remarkable adsorption ability on MB besides the degradation according to our previous reports [30], RB was also used as a mimetic pollutant to further explore the photocatalytic activity of the as-prepared TiO<sub>2</sub>NTs composites under visible light. As shown in **Figure 4b**, after a 7 hours irradiation under visible light, 74% of RB were degraded by the sample CDs-TiO<sub>2</sub>-TiO<sub>2</sub>NTs. That is to say, no matter the degradation of MB under UV light, or RB under visible light, the CDs-TiO<sub>2</sub> nanocomposites anchored TiO<sub>2</sub>NTs exhibited obvious advantages.



**Figure 4.** UV-vis absorption monitoring the degradation of (a) MB (664 nm) and (b) RB (554 nm) with CDs-TiO<sub>2</sub>-TiO<sub>2</sub>NTs.

The photocatalytic efficiency was dependent on the quantity of "reaction centers" participated in the photo-degradation process when the other conditions were equal. While the fine nano-hybrid and tight integration of CDs-TiO<sub>2</sub> could help for the transfer of photogenerated electrons efficiently, and then reduce the recombination rate of electron-hole pairs greatly. Obviously CDs-TiO<sub>2</sub> nanocomposites were easier to anchor on the TiO<sub>2</sub> nanotubes in the initial amorphous state (TiO<sub>2</sub>NTs-0). As a result, the introduction of CDs, fine nano-hybrid of CDs and TiO<sub>2</sub>, together with the abundant decoration of CDs-TiO<sub>2</sub> on the TiO<sub>2</sub> nanotubes, made CDs-TiO<sub>2</sub>-TiO<sub>2</sub>NTs responsible for their excellent photocatalytic performance on MB and RB under UV or visible light.

#### 4. Conclusions

A modified anodic oxidation method was used to prepare initial amorphous TiO<sub>2</sub>NTs. Then TiO<sub>2</sub>NTs composites were prepared through a designed solvothermal technique. The crystallinity of TiO<sub>2</sub>, introduction of CDs-TiO<sub>2</sub> could be finished in the one-step solvothermal routine without any extra annealing treatments in advance. CDs-TiO<sub>2</sub> nanocomposites seemed to be easy to anchor on the TiO<sub>2</sub> nanotubes. So the introduction of CDs, fine nano-hybrid of CDs and TiO<sub>2</sub>, together with the abundant decoration of CDs-TiO<sub>2</sub> on the TiO<sub>2</sub> nanotubes, made CDs-TiO<sub>2</sub>-TiO<sub>2</sub>NTs responsible for their excellent photocatalytic performance on MB and RB under no matter UV or visible light, which would probably be an outstanding catalyst for practical applications.

#### 5. Acknowledgements

The authors gratefully acknowledge the support for this work from the Tianjin Sciences Foundation [16JCQNJC03100] and National Natural Science Foundation of China (Grant 51502345).

#### 6. References

- [1] Chen X. B., Shen S. H., Guo L. J. and Mao S. S. 2010 Chem. Rev. 110 6503.
- [2] Chen X., Liu L., Yu P.Y., Mao S.S. 2011 Science 331 746.
- [3] Kudo A., Miseki Y. 2009 Chem. Soc. Rev. 38 253.
- [4] Wang M., Ioccozia J., Sun L., Lin C., Lin Z. 2014 Energy Environ. Sci. 7 2182.



- [5] Zhao W., Ma W., Chen C., Zhao J., Shuai Z. 2004 J. Am. Chem. Soc. 126 4782.
- [6] Lu Y., Yu H., Chen S., Quan X., Zhao H. 2012 Environ. Sci. Technol. 46 1724.
- [7] Su J., Yu H., Quan X., Chen S., Wang H. 2013 Appl. Catal. B: Environ. 138 427.
- [8] Su J., Yu H., Chen S., Quan X., Zhao Q. 2012 Sep. Purif. Technol. 96 154.
- [9] O'regan B., Grätzel M. 1991 Nature 353 737.
- [10] Crossland E.J., Noel N., Sivaram V., Leijtens T., Alexander-Webber J.A., Snaith H.J. 2013 Nature 495 215.
- [11] Gong J., Li Y., Hu Z., Zhou Z., Deng Y. 2010 J. Phys. Chem. C 114 9970.
- [12] Lu R., Zhou W., Shi K., Yang Y., Wang L., Pan K., Tian C., Ren Z., Fu H. 2013 Nanoscale 5 569.
- [13] Deepagan V. G., You D. G., Um W., Ko H., Kwon S., Choi K. Y., Yi G., Lee J. Y., Lee D. S., Kim K., Kwon I. C., and Park J. H. 2016 Nano Lett. 16 6257.
- [14] Dhanasekaran P., Selvaganesh S. V. and Bhat S. D. 2017 New J. Chem. 41 2987.
- [15] Yan Y., Han M., Konkin A., Koppe T., Wang D., Andreu T., Chen G., Vetter U., Morante J. R. and Schaaf P. 2014 J. Mater. Chem. A 2 12708.
- [16] Wang J. and Lin Z. 2010 Chem. Mater. 22 579.
- [17] Xie G. C., Zhang K., Guo B. D., Liu Q., Fang L. and Gong J. R. 2013 Adv. Mater. 25 3820.
- [18] Zhang N., Zhang Y. H. and Xu Y. J. 2012 Nanoscale 4 5792.
- [19] Kim H. I., Moon G. H., Satoca D. M., Park Y. and Choi W. 2012 J. Phys. Chem. C 116 1535.
- [20] Mor G.K., Varghese O.K., Paulose M., Grimes C.A. 2005 Adv. Funct. Mater. 15 1291.
- [21] Gong D., Grimes C.A., Varghese O.K., Hu W., Singh R.S., Chen Z., Dickey E.C. 2001 J. Mater. Res. 16 3331.
- [22] Rani S., Roy S. C., Paulose M., Varghese O. K., Mor G. K., Kim S., Yoriya S., LaTempa T. J. and Grimes C. A. 2010 Phys. Chem. Chem. Phys. 12 2780.
- [23] Rho W. Y., Kim H. S., Kim H. M., Suh J. S. and Jun B. H. 2017 New J. Chem. 41 285.
- [24] Baker S. N. and Baker G. A. 2010 Angew. Chem. Int. Ed. 49 6726.
- [25] Zhang X., Wang F., Huang H., Li H., Han X., Liu Y. and Kang Z. 2013 Nanoscale 5 2274.
- [26] Li H., He X., Kang Z., Huang H., Liu Y., Liu J., Lian S., Tsang C. H. A., Yang X. and Lee S.-T. 2010 Angew. Chem. 49 4430.
- [27] Wang J., Gao M. and Ho G. W. 2014 J. Mater. Chem. A 2 5703.
- [28] Martins N. C.T., Ângelo J., Girão A. V., Trindade T., Andrade L., Mendes A. 2016 Appl. Catal. B: Environ. 193 67.
- [29] Su J., Zhu L., Geng P., Chen G. 2016 J. Hazard. Mater. 316 159.
- [30] Li F., Tian F., Liu C., Wang Z., Du Z., Li R., Zhang L. 2015 RSC Adv. 5 8389.